

## REACTIONS OF PROPANE ON HYDROUS METAL OXIDE-SUPPORTED CATALYSTS

Zhentao Feng and Rayford G. Anthony  
Department of Chemical Engineering, Texas A&M University  
College Station, TX 77843

Keywords: propane, dehydrogenation, metal oxide

### INTRODUCTION

There are strong economical incentives today to develop catalysts for the selective conversion of light paraffins, especially propane. Formation of propylene, aliphatics or aromatics is favorable. Previous work has shown catalytic conversion of propane on HZSM-5 (Inui and Okazumi, 1984; Kitagawa et al., 1986; Scurrrell, 1988). The main products are benzene, toluene and xylenes. In this work, a relatively new type of catalyst is prepared for the reaction of propane, i.e., hydrous metal oxides.

Hydrous metal oxides were first used for waste water treatment and direct coal liquefaction (Stephens et al., 1985). Research on these materials identified several properties that might make hydrous metal oxides useful as catalyst supports. They include high surface area, large ion exchange capacity, dual ion exchange properties for cation and anion, and strong thermal stability (Lehto, 1987). This study employed hydrous metal oxides as catalyst supports for the synthesis of catalysts for the propane transformation.

### EXPERIMENTAL

**Catalysts.** Sol-gel method was used to prepare two different types of hydrous metal oxides, i.e., hydrous silicon titanium oxide and hydrous zirconium oxide. The main procedure followed the patent by Dosch et al. (1985):

Tetraisopropyl titanate was mixed with tetraorthoethyl silicate to get a clear solution. Then slowly add the alkoxide mixture into a 10 wt% methanol solution of sodium hydroxide to get a very thick soluble intermediate. The intermediate was rapidly added to a solution of 1:10 water and acetone. The slurry was continuously stirred until it was homogenized. Filter the mixture and rinse with acetone. Collect the precipitate and dry it in vacuum at 80 °C overnight. This procedure was used to prepare hydrous silicon titanium oxide.

Hydrous zirconium oxide was synthesized by the same procedure, except that zirconium propoxide and potassium hydroxide were used. These two types of hydrous metal oxides were incorporated with Mo, Ni, Pd or Zr via ion exchange. After ion exchange, the catalysts were treated with sulfuric acid and then calcined in air at 540 °C.

**Activity Tests.** Activities of the catalysts were determined by their performance in the reactions of propane. Reactions were carried out isothermally in a Pyrex reactor under atmospheric pressure. Reaction temperature was 600 °C. The feed was 20% propane in nitrogen. Propane weight hour space velocity was 1.5 to 1.9. Composition of products was obtained with two GCs using a flame ionization detector and a thermal conductivity detector, respectively.

## RESULTS

*Characterization of Catalysts.* Hydrous metal oxides as prepared were amorphous materials with 30% to 35% volatile. The surface areas of hydrous silicon titanium oxide and hydrous zirconium oxide were 390 m<sup>2</sup>/g and 260 m<sup>2</sup>/g, respectively. The pore volume was 0.6 cc/g with pore diameters in the range of mesopores. After ion exchange, the weight percent of Pd, Mo, Ni and Zr in the catalysts were 0.52%, 15%, 1.4% and 14% respectively based on dry weight. After calcination, hydrous silicon titanium oxide and hydrous zirconium oxide changed to their oxide forms, i.e., silica, titania and zirconia. X-ray diffraction showed that titania was predominately anatase with a small amount of rutile, while the phase of zirconia was cubic.

NaOH titration and temperature programmed desorption of ammonia experiments showed that the catalysts synthesized were weak acidic materials. Zirconia supported catalysts had higher acidity than the corresponding silica titania catalysts. Figure 1 is the ammonia TPD of Pd on zirconia and Pd on silica titania. Most of the ammonia desorbed below 250 °C, which indicates the absence of strong acid sites.

*Activity Tests.* Figure 2 is the summary of the activity tests on the catalysts. Dehydrogenation was the main reaction of propane and propylene was the largest reaction product. The change of propylene selectivity at different levels of propane conversion is shown on the figure. For silica titania supported catalysts, propane conversion ranged from 10% to 20% and propylene molar selectivity from 55% to 70%. For most zirconia supported catalysts, the conversion of propane was higher, up to 30% to 47%.

Besides propylene, the product consisted of methane, ethane, ethylene, small amounts of aromatics and C<sub>4</sub> to C<sub>6</sub> aliphatics. Figure 3 is the product distribution of propane reaction on silica titania supported molybdenum. Molar selectivities to light hydrocarbons ranged from 5% to 15% without significant change with time on stream.

Figure 4 shows the effects of active metals on propane conversion. The three catalysts were Pd, Mo and Ni supported on zirconia. The comparison indicated that palladium was the most active among these three metals.

## DISCUSSION

From thermodynamic equilibrium point of view, propane converts to light hydrocarbons (methane, ethane, etc.) and aromatics much more favorably than to propylene. The results of this study showed just the opposite. Propylene was the main reaction product. Previous work (Riley and Anthony, 1986) on alkane transformation over HZSM-5 showed the formation and reactions of carbonium ions on the catalysts surface. On strong acid sites, carbonium ions would undergo cracking and aromatization reactions forming methane, ethane and aromatics. However, the catalysts in this study are weak acidic materials, consequently the formation and reactions of carbonium ions are less favorable. The mechanisms of propane

reaction on these catalysts are hydride abstraction on the dispersed metals. Hydride abstraction of propane produces propylene and hydrogen. Palladium has relatively strong interactions with hydrides and hence shows higher activity, which coincides with the experimental results. Beside hydride abstraction, carbonium ion formation and reactions, though not as important as that on zeolite, also contributes to the reaction. Zirconia supported catalysts have stronger acidity than titania supported ones, and hence higher amount of light hydrocarbons and aromatics are produced.

The equilibria conversion of propane to propylene at 600 °C is about 45%. Some catalysts in this study achieved about 35% to 45% conversion. Most catalysts showed high selectivity to propylene (about 60%). Therefore, hydrous metal oxides show considerable potential for the synthesis of catalysts for propane dehydrogenation.

#### ACKNOWLEDGEMENTS

The synthesis of the palladium catalysts by Dr. R.G. Dosch of Sandia National Laboratories is very much appreciated. The financial support of Texaco, Inc for the Texas A&M Research Foundation Project 6448 is also gratefully appreciated.

#### REFERENCES

1. Dosch, R.G., H.P. Stephens, and F.V. Stool, U.S. Patent 4,511,455, 1985.
2. Feng, Z., M.S. Thesis, Texas A&M University, 1991.
3. Inui, T., and Okazumi, "Propane Conversion to Aromatic Hydrocarbons on Pt/H-ZSM-5 Catalysts," *Journal of Catalysis*, 90, 366, 1984.
4. Kitagawa, H., Y. Sendoda, and Y. Ono, "Transformation of Propane into Aromatic Hydrocarbons over ZSM-5 Zeolites," *Journal of Catalysis*, 101, 12, 1986.
5. Lehto, J., "Sodium Titanate for Solidification of Radioactive Waste - Preparation, Structure and Ion Exchange Properties," Academic Dissertation, Department of Radiochemistry, University of Helsinki, 1987.
6. Riley, M.G., and R.G. Anthony, "Transition-State Selectivity in the Cracking of N-Heptane over Modified ZSM-5 Catalysts," *Journal of Catalysis*, 100, 322, 1986.
7. Scurrell, M.S., "Factors Affecting the Selectivity of the Aromatization of Light Alkanes on Modified ZSM-5 Catalysts," *Applied Catalysis*, 41, 89, 1988.
8. Stephens, H.P., R.G. Dosch, and F.V. Stool, "Hydrous Metal Oxide Ion Exchangers for Preparation of Catalysts for Direct Coal Liquefaction," *I&EC Proc. Res. Dev.*, 24, 15, 1985.

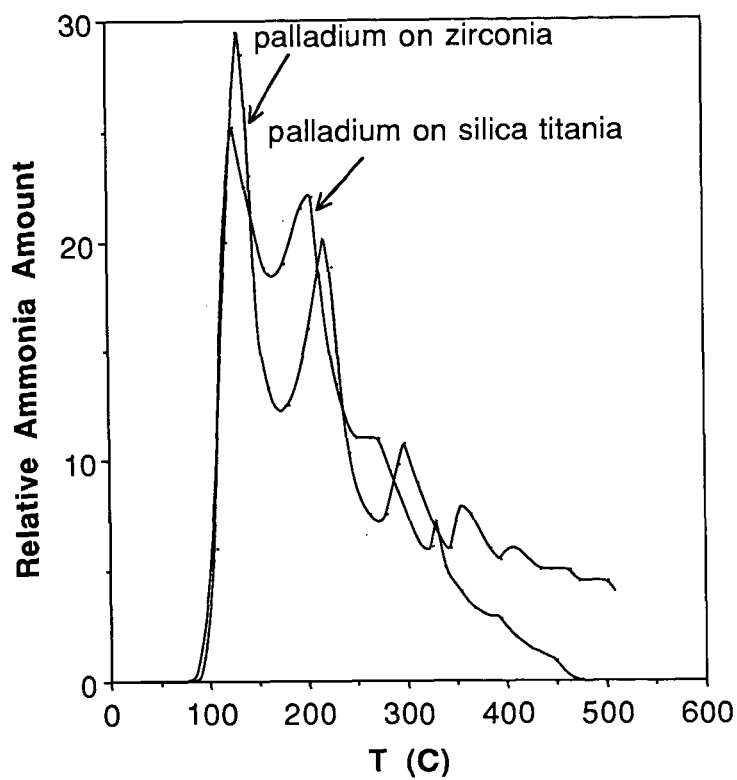


Figure 1. Ammonia TPD of Catalysts

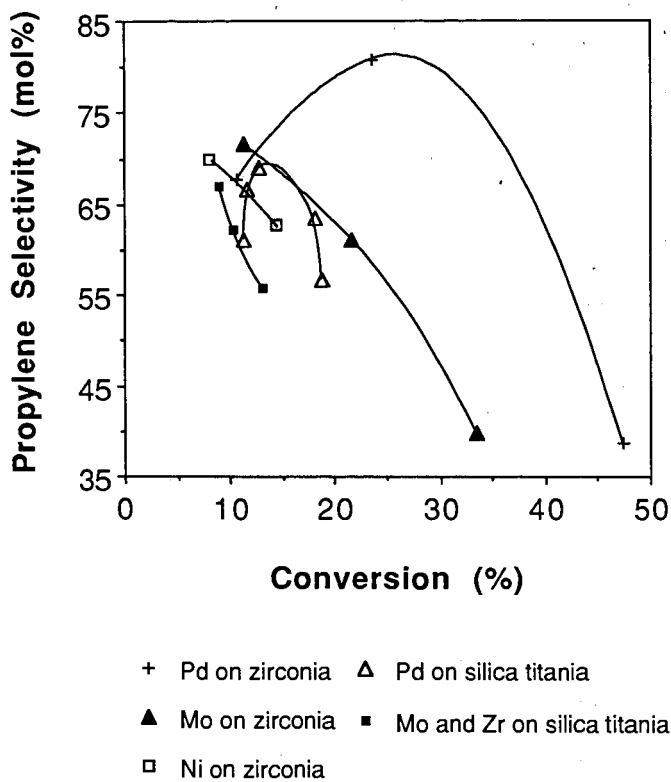


Figure 2. Propylene Selectivity at Different Levels of Propane Conversion

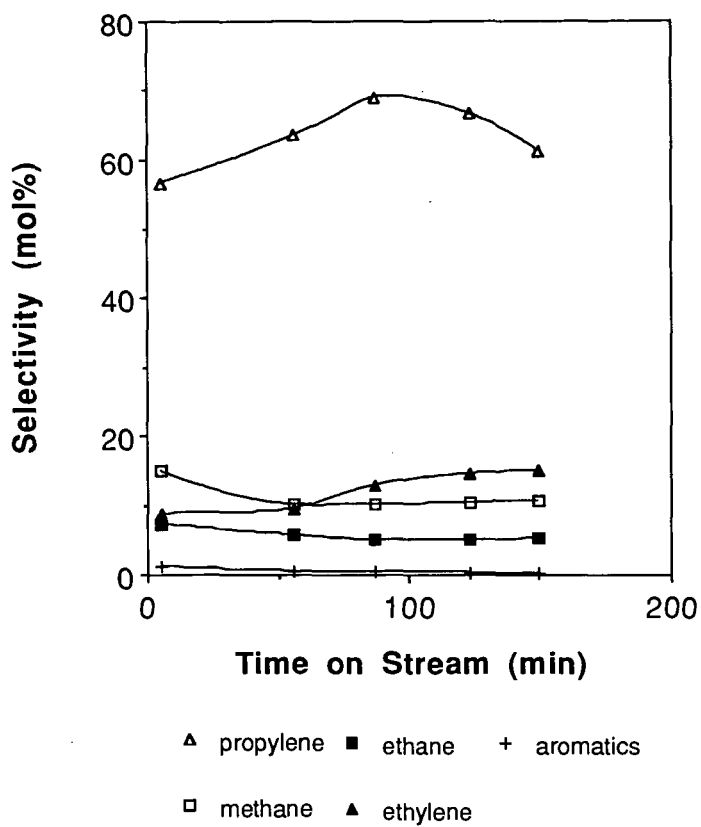


Figure 3. Product Distribution of Propane Transformation for Mo on silica titania

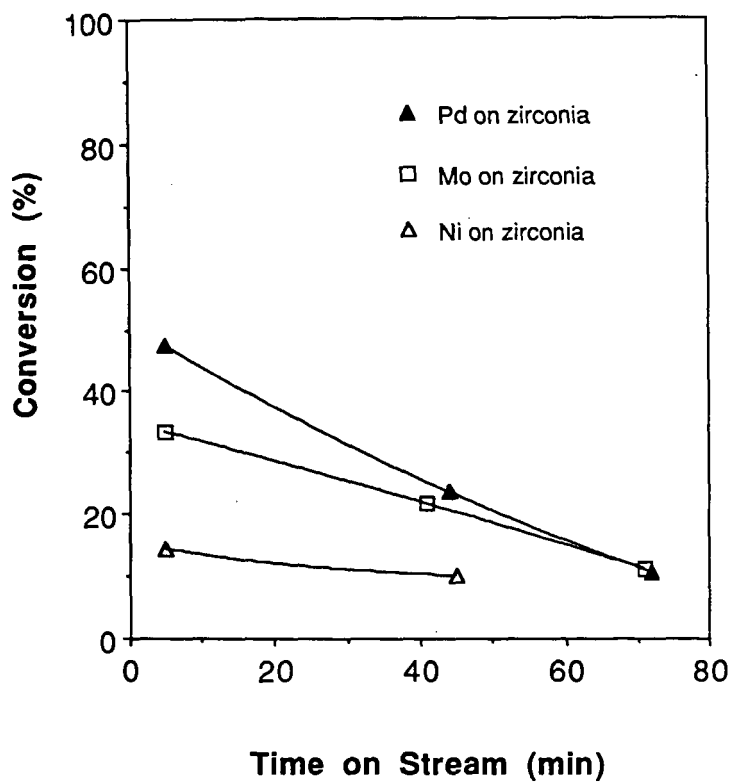


Figure 4. Comparison of Different Active Metals